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Sachdev et al.

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(54) AQUEOUS CLEANING OF PASTE RESIDUE

(75) Inventors: Krishna G. Sachdev, Hopewell Junction; James N. Humenik, LaGrangeville; John U. Knickerbocker, Hopewell Junction; Glenn A. Pomerantz, Kerkhookson, all of NY (US)

(73) Assignee: International Business Machines Corporation, Armonk, NY (US)

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(56) References Cited

U.S. PATENT DOCUMENTS

4,039,371 * 8/1977 Brunner et al. 156/668
4,362,486 12/1982 Davis et al.
4,483,040 11/1984 Magee et al.
5,221,362 6/1993 Porta et al.
5,264,047 11/1993 Winston et al.
5,279,756 1/1994 Savio et al.
5,286,403 2/1994 O'Dwyer et al.

5,464,553 11/1995 Winston et al.
5,466,389 * 11/1995 Ilardi et al. 252/156
5,498,293 * 3/1996 Ilardi et al. 134/3
5,575,857 11/1996 Linski et al.
5,593,504 1/1997 Cala et al.
5,643,818 7/1997 Sachdev et al.
5,679,169 * 10/1997 Gonzales et al. 134/1.3
5,705,089 * 1/1998 Sugihara et al. 252/79.1
5,855,811 * 1/1999 Grieger et al. 252/79.3
5,858,109 * 1/1999 Hymes et al. 134/2
5,989,353 * 11/1999 Skre et al. 134/2
6,017,862 * 1/2000 Doyel et al. 510/163
6,033,993 * 3/2000 Love, Jr. et al. 438/745
6,060,439 * 5/2000 Doyel et al. 510/164

FOREIGN PATENT DOCUMENTS

40730503A * 11/1995 (JP).

* cited by examiner

Primary Examiner—Margaret Einsmann

Assistant Examiner—Gregory E Webb

(57) ABSTRACT

This invention relates to an aqueous cleaning method for removal of metal-organic composite paste residue from the surface of components, such as, screening masks, associated paste screening equipment, substrates, to name a few. The invention is particularly concerned with aqueous alkaline cleaning solutions comprising alkali metal salt and/or quaternary ammonium salt of an organic acid preferably α -hydroxy carboxylic acid in the presence of excess alkali and optionally a surface active agent for use in cleaning components, such as, screening masks, associated screening equipment, substrates, etc., which are used in the production of electronic components.

17 Claims, No Drawings

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AQUEOUS CLEANING OF PASTE RESIDUE

FIELD OF THE INVENTION

This invention relates to an aqueous cleaning method for removal of metal-organic composite paste residue from the surface of components, such as, screening masks, associated paste screening equipment, substrates, to name a few. The invention is particularly concerned with aqueous alkaline cleaning solutions comprising alkali metal salt and/or quaternary ammonium salt of an organic acid preferably α -hydroxy carboxylic acid in the presence of excess alkali and optionally a surface active agent for use in cleaning components, such as, screening masks, associated screening equipment, substrates, etc., which are used in the production of electronic components.

BACKGROUND OF THE INVENTION

In the fabrication of ceramic substrates or ceramic chip carriers, conductive metal pattern for wiring and via metallurgy on substrate is defined by screening metal-polymer composite paste on green sheet by screening through a contact mask, such as a metal mask with closely spaced fine dimension etched pattern. Paste screening through such masks leaves paste residue on the mask surface as well as on the side walls of the mask features. This residue must be removed after one or more screening passes in order to assure consistent quality defect-free screened pattern.

Standard process for ceramic substrate production involves green sheet casting of ceramic slurry on a carrier, green sheet blanking, via punch, circuit personalization by screening of conductive paste through a mask screen, followed by singulation/sizing, inspect/collate/register, stack and lamination, binder burn-off and sintering operation.

The ceramic slurry typically comprises ceramic filler, polymer binder, solvent vehicle and dispersing agent.

The conductive pastes commonly used in multilayer ceramic (MLC) technology are dispersions of metal powder, polymer binder, and a high boiling solvent system along with suitable surfactants, dispersants, and thickening agents to obtain desired screening characteristics.

Commonly used metal fillers are molybdenum, copper, tungsten, and nickel in conjunction with polymer binders of the type, ethyl cellulose, acrylate polymers as poly(methyl methacrylate), poly(ethyl methacrylate) and related systems, and polyhydrocarbons based thermoplastic resins, which are all hydrophobic polymer systems.

Representative high boiling solvents used in metal-polymer dispersions are ester-alcohol such as 2,2,4-trimethylpentane diol-1,3-monoisobutyrate (Texanol), glycol ether type solvents, such as, di(ethyleneglycol) monomethyl ether, di(ethyleneglycol) monobutyl ether acetate or butyl carbitol acetate (BCA), di(propyleneglycol) monomethyl ether, di(propylene glycol) monobutyl ether and the like.

Solids component of the pastes used typically comprise between about 70 to about 85% by weight of metal filler, between about 1 to about 5% of organic binder and other necessary organic additives, and the balance constituting the solvent vehicle system. Depending on the binder-solvent system used in paste formulations, the paste can be polar or non-polar, hydrophilic or oleophilic and thus having different wetting characteristics for water-based cleaning and also to having different interface interactions and adhesion to various metal mask surfaces. Selection of a particular paste type in terms of the metal filler and its particle size

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distribution, the polymer binder and the solvent system is dictated by the requirement of the desired circuit pattern, conductivity of metallurgical pattern, and compatibility of the paste with the ceramic green sheet material.

In high throughput screening in the production of ceramic substrates, mask cleaning has been carried out with organic solvents in a real time operation to provide cycle time compatibility with manufacturing screening and cleaning requirements, such as described in U.S. Pat. No. 4,362,486 (Davis) and U.S. Pat. No. 4,483,040 (Magee), assigned to International Business Machines Corporation, Armonk, USA, and the disclosures of which are incorporated herein by reference.

With organic solvent-based cleaning, there are issues of flammability or combustibility, chemical safety, and waste disposal and associated cost, and therefore, aqueous cleaning is generally preferred for high volume production environment.

U.S. Pat. No. 5,221,362 (Porta) describes non-halogenated aqueous degreasing compositions based on mixture of alkanolic acid including hydroxy alkanolic acid, straight chain alkanol or an alkyl ester and water for use in removing inks and cleaning printed circuit boards.

U.S. Pat. No. 5,264,047 (Winston) describes aqueous cleaning compositions comprising alkaline salts, organic adjuvants, and a low foam hydrotrope comprised of alkali metal salt of carboxylic acids having a chain length of 7-13 carbon atoms. These compositions are used in removing soldering flux and other residue from printed wiring boards.

U.S. Pat. No. 5,279,756 (Savio) discloses non-phosphate machine dishwashing detergents, such as, alkali metal carbonate, bicarbonate, and hydroxy carboxylic acid as complexing agent.

U.S. Pat. No. 5,286,403 (O'Dwyer) describes phase-stable, aqueous cleaning concentrates containing an inorganic acid and organic acid with surfactants for cleaning floor tiles.

U.S. Pat. No. 5,464,553 (Winston) is concerned with aqueous cleaning compositions comprising alkali metal salt as carbonate/bicarbonate, organic adjuvants, and a hydrotrope for solder flux removal.

U.S. Pat. No. 5,575,857 (Lunski) is concerned with aqueous alkaline cleaning concentrate for removing inorganic salt or scale from metal surface, the cleaning solution consisting of sodium and potassium carbonate salt and a hydrotrope as sodium, potassium, ammonium, and alkanolammonium salt of sarcosinate.

U.S. Pat. No. 5,593,504 (Cala) describes method of cleaning solder paste from substrates with an aqueous cleaner, such as, alkali metal carbonate, a surfactant, alkali metal silicate, and a stabilizer for silicate, to provide a safer replacement for alcohol solvents.

As stated earlier, this invention is concerned with cleaning masks and associated equipment used in screening conductive paste onto green sheet in the manufacture of multilayer ceramic substrates. The invention is also applicable to cleaning metal stencils used in the deposition of solder paste pattern on substrates. This invention is especially concerned with aqueous cleaning of screening masks with water-based cleaning compositions that are, preferably biodegradable and/or are compatible with standard wastewater treatment methods.

According to this invention, it has been found that alkaline solutions comprising α -hydroxy acid salts, particularly, sodium, potassium, and tetraalkyl ammonium salt of lactic

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acid, aspartic acid, citric acid, gluconic acid, glycolic acid, tartaric acid, and related systems in the presence of excess alkali and optionally a surface active agent provide highly effective cleaning solutions for removing screening paste residue from metal masks, such as, Cu, Cu/Ni, Cu/Ni/Cu, Mo, stainless steel, to name a few. These metal masks can be electroform masks, stencils, etc.

It has been found that aqueous solution of lactic acid, aspartic acid and/or gluconic acid, sodium and/or potassium salt, or tetramethylammonium salt with pH adjusted to between 11.5-12.8 by adding excess alkali, and optionally a low foam non-ionic and/or an amphoteric surfactant or an ionic surfactant provides excellent cleaning system for screening masks to remove Mo, Cu, Cu/Ni, and tungsten based polar and non-polar pastes using pressure spray or ultrasonic agitation. In high pressure cleaning of screening masks in the MLC production using 130-180 psi spray pressure and 140-170° F. solution temperature, cycle time for mask cleaning can be less than 20 seconds, on an automated screening and cleaning tool. These compositions are also found effective in cleaning solder paste residue from the metal stencils and screens. Such pastes generally consists of solder filler, such as, Pb/Sn eutectic, Pd/Sn/Pd, Ag/Pd, Pb/In, Sn/Bi, Sn/In, in organic carrier/solvent and fluxing agent, such as, rosin-based flux, organic acids, to name a few.

PURPOSES AND SUMMARY OF THE INVENTION

The invention provides novel aqueous alkaline cleaning compositions based on α -hydroxy carboxylic acid salts in the presence of excess alkali, and method for cleaning components, such as, screening masks used in the delineation of conductive pattern onto ceramic green sheet in the production of multilayer ceramic substrates. The invention is also applicable to cleaning solder paste from metal stencils. The aqueous cleaning method according to this invention provides an alternative to organic solvent-based cleaning while maintaining the cycle time requirement for high throughput production with no impact on product reliability.

Therefore, one purpose of the present invention is to provide an alternate method for cleaning mask screens used in the production of ceramic substrates that provides effective cleaning with process reproducibility and is compatible with the cycle time requirement in manufacturing operation.

Another purpose of this invention is to provide an aqueous cleaning method for removing solder paste residue from metal stencils and screens.

Yet another purpose of the present invention is to provide an aqueous cleaning composition using salt of hydroxy carboxylic acids, particularly lactic acid, aspartic acid, citric acid, tartaric acid mandelic acid, gluconic acid, glycolic acid, and combination thereof, in excess alkali, and optionally low foam surfactants, preferably amphoteric and/or non-ionic surfactants, and ionic surfactant. The composition can also contain other additives as corrosion inhibitor and softener as alkali metal silicate, alkali metal phosphate, such as, sodium tripolyphosphate (STPP).

Still another purpose of this invention to provide aqueous alkaline cleaning compositions for efficient removal of Mo, Cu, W, and Cu/Ni-based conductive paste residue from screening masks by using alkali metal salt and/or tetramethylammonium salt of lactic acid and/or aspartic acid and/or gluconic acid, with excess alkali for pH adjustment in the range of between about 11.5 and about 12.8.

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Still yet another purpose of this invention to provide a method of mask cleaning with α -hydroxy carboxylic acid salt containing aqueous alkaline cleaning compositions with pressure spray and/or ultrasonic agitation techniques.

Yet another purpose of this invention is to provide an aqueous cleaning method for screening masks where the dissolved metals and organics in the waste water are readily removed by standard treatment methods while the active ingredient in the cleaning solution are mostly biodegradable or removable by standard water treatment methods and thus the waste water can be safely discharged.

Therefore, in one aspect this invention comprises an aqueous alkaline cleaning composition for removing paste residue from a component comprising, at least one water soluble salt of hydroxy carboxylic acid, water, at least one organic and/or inorganic base, and optionally a surface active agent.

DETAILED DESCRIPTION OF THE INVENTION

The aqueous cleaning compositions according to this invention are alkaline solutions of pH in the range of between about 11.5 and about 12.8, and are comprised of α -hydroxy carboxylic acid sodium and/or potassium or quaternary ammonium salt in aqueous alkali, and optionally a low foam non-ionic, ionic, and/or amphoteric surfactant. Preferred hydroxy carboxylic acid salts are derived from lactic acid, aspartic acid, citric acid, gluconic acid, tartaric acid and combinations thereof, which is neutralized with alkali metal hydroxide or alkali metal carbonate and/or bicarbonate or sesquicarbonate, and/or a quaternary ammonium hydroxide, such as, tetramethylammonium hydroxide, tetraethylammonium hydroxide, or 2-hydroxyethyltrimethylammonium hydroxide (Choline hydroxide), and combination thereof. Sodium lactate, a hydroxy carboxylic acid salt useful for the purpose of this invention is available commercially under the trade name 'Lacoline' as 70-80% in water. Corresponding potassium and tetramethylammonium salts of lactic acid and/or aspartic acid are prepared by neutralizing aqueous solution of the organic acid with stoichiometric amount of aqueous alkali and then adding excess alkali to bring to pH preferably in the range of between about 11.5 to about 12.8, preferably between about 12.1 and about 12.5.

Preferred cleaning solutions for cleaning MLC screening paste from masks according to this invention are based on tetramethylammonium lactate (TMA-lactate) and/or TMA-gluconate or a combination of the corresponding sodium or potassium and TMA-salts of lactic acid, aspartic acid and gluconic acid, with alkali in excess of stoichiometry to obtain pH in the range of between about 12.1 and about 12.5.

Alternate hydroxy carboxylic acid salts which can also be used according to this invention include salt of citric acid as trisodium citrate, sodium tartrate, sodium hydrogentartrate, potassium tartrate, potassium hydrogentartrate, mandelic acid salts, and the corresponding tetramethylammonium salts.

Surfactants may also be added which can be non-ionic, ionic, or amphoteric and combination thereof.

Low foam amphoteric surfactants preferred according to this invention are based on alkylated carboxyalkyl tertiary amines of the type $R-N(CH_2CH_2COOxy)_2$, where R=organic radical represented by C_nH_{2n+1} , n=8-12, x=H, and y=M⁺, M being alkali metal ion, typically, Na, K, ions, or organic ammonium ion as quaternary ammonium ion. Representative amphoteric surfactants of this class include

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Amphoteric-N, Amphoteric AO-400 and AO-14-2 (Tomeh Products), betaine derivatives as coco-imidopropyl betaine and related materials which can also be used in conjunction with non-ionic and/or ionic surfactants. Low foam non-ionic surfactants that can be used alone or in combination with amphoteric surfactant are: linear primary alcohol ethoxylates, particularly those which are biodegradable, such as with trade name designations: Neodol (Shell Corp.), Pluronic 25R2, Plurafac RA 30, Plurafac A-39 (BASF), Triton DF-12, Triton-54, Triton CF10 and DF-20 (Rohm and Hass) and Polytergent ADL ultra-LF, and SLF-18 B series of biodegradable surfactants (Olin Corp.). In addition, fluoroalkylene (polyoxyalkylene) surfactants, such as, 'Fluorads' (3M Corp.) of low foam type such as FC-171, FC-129, FC-170C, and FC-120 can also be used. Other non-ionic surfactants found effective according to this invention include polyalkyl glycoside-based as Glucopon LF-1 and related alkyl polysaccharide ethers (Henkel/Emery).

Various ionic surfactants useful for the purpose of this invention have been found to be alkyl alcohol and ethoxylated alcohol sulfates and sulfonates, as sodium lauryl sulfate, alkylarylsulfates and sulfonates, such as, sodium dodecylbenzene sulfonate.

Representative aqueous cleaning compositions according to this invention consist of:

(a) between about 0.5 and about 5.0 (wt %) solution comprising lactic acid and/or gluconic acid, sodium salt and excess NaOH or KOH or tetramethylammonium hydroxide to adjust pH in the range of between about 11.9 and about 12.7. The solution may also contain between about 0.03 and about 0.2% AO-400 as an amphoteric surfactant; and/or 0.05 to about 0.20 weight percent of a non-ionic surfactant, preferably among the biodegradable surfactant based on ethoxylated alcohols, alkyl polyglycosides.

Alternatively, non-ionic surfactants of the type octylphenoxypolyethoxyethanol such as Triton-405, and Triton X-100, can also be used.

(b) tetramethylammonium salt of lactic acid (TMA-lactate) formed by neutralization of lactic acid solution in water with aqueous tetramethylammonium hydroxide (TMAH) and additional TMAH to adjust pH to between about 12.0 and about 12.5 and having between about 0.5 and about 3.0% (wt %) of combined active ingredients TMAH salt and excess alkali, and other additives, the balance being water;

(c) between about 0.4 and about 1.0% lactic acid and/or gluconic acid salt obtained by neutralization of the acid form with NaOH, KOH, Na_2CO_3 , sodium sequecarbonate, and/or TMAH and additional alkali, between about 0.3 and about 1.0% (wt %) to adjust pH in the range of between about 12.2 and about 12.8, and AO-400 amphoteric surfactant in combination with between about 0.05 to about 0.15 wt %, and between about 0.02 to about 0.10 wt % ethoxylated alcohol sulfate as surfactant, such as, Standapol-LF (Henkel/Emery), and primary alcohol ethoxylate as a non-ionic surfactant.

This invention provides an environmentally friendly, low cost, non-hazardous, non-toxic, and non-flammable replacement of solvent-based cleaning utilizing active ingredients that can be obtained through synthesis or are derived from natural sources. Lactic acid occurs in sour milk as a result of lactic acid bacteria, in molasses, and in many fruits. It is obtained by the fermentation of carbohydrates with *bacillus*

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acidi Lacti. Sodium lactate is commercially available (trade name 'Lacoline') as between about 70 and about 80% in water. Sodium gluconate is also commercially available as solution in water. Lactate salts are used in shampoos, liquid soaps, cleansing creams and other personal care products. Lactates and aspartates are readily biodegradable.

Trisodium citrate water solution has pH about 8 and sodium tartrate, pH between about 7 and about 9.

Another advantage of this invention is that the wastewater can be safely discharged after removing dissolved metal and paste organics and inorganics from the effluent from mask cleaning process.

It has been found that with Mo and W pastes, there is varying level of dissolved metal remaining in the effluent after all the suspended solids are filtered out. The dissolved Mo and W in effluent from Mo and W pastes cleaning with alkaline TMA-lactate and/or Na-lactate and/or K-lactate solutions can be easily removed by ion exchange method or by adsorption on filter-aid/activated charcoal filter bed. A method of Mo and W removal from lactate-based effluent involves filtering the effluent from cleaning paste residue using a series of filters to minimum of about 0.2 micron cartridge filter or about 500 Å membrane filter, neutralizing the filtrate with mineral acid, and filtering through Celite filter-aid and activated charcoal bed. In this treatment, about 50% reduction in dissolved Mo could be obtained, for example, initial Mo concentration of 94 ppm in the effluent was reduced to about 52 ppm after filter-aid/activated charcoal treatment. For more complete removal of dissolved metals, ion-exchange method can be used.

EXAMPLES

The following examples are intended to further illustrate the invention and are not intended to limit the scope of the invention in any manner.

Example 1

An aqueous cleaning solution comprising between about 1.7 to about 1.8 wt % of active ingredient having pH of between about 12.1 to about 12.3, was prepared by mixing about 242 g of about 85 weight percent lactic acid solution with about 1200 ml of 10 wt % NaOH aqueous solution and about 80 ml of 25 wt % aqueous tetramethylammonium hydroxide (TMAH) in deionized water to make up about 5 gallons. Metal masks carrying conductive screening paste residue on about 7 to about 8 inch square active area mask, after screening operation were cleaned by pressurized spray of heated cleaning solution at between about 140 to about 150° F., at between about 60 and about 70 psi, for between about 45 and about 60 seconds, which consumed between about 2500 and about 3500 ml of solution for each mask. The spray cleaning step was immediately followed by water spray rinse at between about 120 and about 130° F. under pressure, and dry conditions. Various types of conductive pastes on Mo and Cu/Ni and Cu/Ni/Cu electroform masks included those having Mo, Cu, W, or Cu-Ni filler in ethyl cellulose binder and 2,2,4-trimethylpentane diol-1, 3monoisobutyrate (Iexanol) as solvent along with other necessary additives comprising surfactant/dispersant and rheology control additives. Ultrasonic cleaning of screening masks at about 40 kHz frequency, with this solution at between about 140 and about 150° F. also provided effective cleaning within about 30 to about 60 seconds of immersion with ultrasonic agitation followed by water rinse and dry by blowing hot air. Different types of paste residue on masks that were cleaned included pastes with Mo, W, Cu, Cu/Ni

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metal filler with and without ceramic filler in ethyl cellulose/Texanol binder/solvent system in conjunction with hydrogenated Castor Oil as a thickening agent and sarcosinate as a surfactant was readily removed from metal masks which included Mo, Cu/Ni and Cu/Ni/Cu electroform masks.

Highly efficient cleaning of Mo, Cu, and W paste residue from Mo and electroform screening masks was obtained with this solution at between about 150 and about 170° F. using a multi-nozzle two-sided pressurized spray cleaning on an automated screening and cleaning tool at between about 150 and about 170 psi pressure requiring less than about 20 seconds for paste residue removal which was immediately followed by pressure spray rinse with hot deionized water and hot air dry. In this automated cleaning process, about 1 gallon of solution was used up for cleaning each mask with the same volume of water in the rinse cycle. Microscopic inspection of the cleaned masks showed complete removal of residue from all areas of mask for all types of pastes which included polar type comprising ethyl cellulose/ester alcohol and ethylene-glycol alkyl ether butyrate as binder-solvent vehicle system, and the non-polar paste residue comprising thermoplastic hydrocarbon resin binder with non-polar ink oil solvent vehicle.

Example 2

An aqueous cleaning solution comprising stoichiometric TMA-lactate salt (tetramethylammonium lactate) and excess TMAH to obtain pH in the range between about 12.3 and about 12.4 was prepared by mixing 100 parts (by volume) of about 1.0 % aqueous TMAH solution with about 125 parts of 1.0% solution of about 85% lactic acid solution in water to form TMA-lactate of 1:1 stoichiometry adding excess TMAH for pH adjustment to desired pH range of between about 12.3 to about 12.4. Mask cleaning with this solution to remove screening paste residue similar to the methods described in Example 1 above using spray or ultrasonic cleaning followed by water spray rinse and dry showed effective removal of residue from various types of pastes on Mo and electroform masks.

Example 3

An aqueous cleaning solution having pH about 12.7 was prepared by combining aqueous solutions of sodium lactate, sodium carbonate, and sodium hydroxide to obtain total solids between about 0.8 and about 1.0% with a relative ratio of 7:1:2 for hydroxide/carbonate/lactate concentration, respectively. Pressure spray cleaning of masks carrying residue from various types of screening pastes with this to solution pre-heated at between about 150 and about 160° F. with standard single-nozzle pressure spray method at about 70 psi and between about 45 and about 60 seconds cleaning time provided complete removal of residue. Subsequent pressure spray rinse with hot water and hot air dry gave clean masks suitable for repeat screening operation.

Example 4

An alkaline cleaning solution of pH about 12.1 and containing about 2.0% active ingredients comprising sodium lactate, excess NaOH, and non-ionic surfactant Triton X-405 and amphoteric surfactant AO-14-2 was prepared by mixing 85% lactic acid solution, about 85 g with about 90 g of about 50% (wt %) NaOH and about 40 g X-405 surfactant (70% active) and about 40 g of AO-14-2 (about 50 percent active) in deionized water to a total solution volume of about 5 gallons. The solution was used for cleaning paste processing parts by ultrasonic cleaning method which showed effective

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removal of all types of paste residue from various paste processing/application parts used in screening process, including paste nozzle, reservoir, shutter and other auxiliary equipment. Typical process involved heating the cleaning solution to between about 150 to about 165° F. in an ultrasonic bath operated at about 40 kHz frequency, immersing the parts for about 5 min without ultrasonic agitation and for about 2-10 min with ultrasonic-on, time with ultrasonic agitation, depending on paste type and extent of residue build-up, removing the parts from the cleaning solution and rinsing with hot DI water and drying by blowing air.

Example 5

To an alkaline sodium lactate solution, about 4 gallons, prepared by treating lactic acid with excess NaOH in deionized water, as described in Example 4, having about 2% solids and pH of between about 12.1 and about 12.2 was combined an alkaline sodium citrate (1 gallon) prepared by adding additional NaOH to citric acid trisodium salt, having about 2% solids and about pH 12.3. The solution was heated at between about 160 and about 170° F. and used for cleaning screening masks and other paste residue carrying screening equipment using pressurized spray cleaning or with ultrasonic agitation followed by water rinse and drying cycle. Cleaning tests with different types of pastes in terms of metal filler, polymer binder, and solvent vehicle which comprised Mo, Cu, W, and Cu/Ni based conductive pastes, some of which also contained ceramic filler, showed complete and efficient removal of paste residue. Cleaning time varied with the conditions used, for example, using a standard single nozzle spray head at between about 60 to about 70 psi and between about 150 to about 160° F. solution temperature, it required between about 40 and about 60 sec spray for paste removal followed by about 30 second water rinse with ultrasonic agitation at about 40 kHz frequency, between about 1 to about 2 min, and mask cleaning on an automated screening and cleaning tool using two sided multi-nozzle spray cleaning at between 140 to about 170 psi spray pressure required only between about 15 to about 20 sec for the cleaning step followed by between about 15 to about 20 second rinse with hot deionized water.

Example 6

An alkaline solution of potassium lactate in water and having a surfactant was prepared by neutralizing lactic acid solution with 10 wt % KOH solution and adding excess KOH, and adding about 0.1 weight percent each of the Amphoteric-AO-400 (Tosoh Products) and glucopon LF-1 (Henkel/Emery), as amphoteric and non-ionic surfactants, respectively, to obtain mixed solution pH about 12.3. This solution contained about 2 wt % potassium lactate with excess KOH added for desired pH, and about 0.1 wt % each of the surfactants as the total active ingredients. Spray cleaning of screening masks at between about 60 and about 70 psi and between about 145 and about 155° F. solution temperature, showed effective removal of residue within about 45 to about 60 sec which was followed by spray rinse with hot water and dry. This solution was also used for ultrasonic cleaning of paste processing parts as described in Example 4.

While the present invention has been particularly described, in conjunction with a specific preferred embodiment, it is evident that many alternatives, modifications and variations will be apparent to those skilled in the art in light of the foregoing description. It is therefore contemplated that the appended claims will embrace any

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such alternatives, modifications and variations as falling within the true scope and spirit of the present invention.

What is claimed is:

1. An aqueous cleaning composition for removing paste residue from a component comprising: at least one water soluble salt of a hydroxy carboxylic acid, water, a surface active agent and a member selected from the group consisting of organic and inorganic base, wherein said surface active agent is selected from the group consisting of biodegradable surfactant based on primary alcohol ethoxylate, alkylpolyglycosides based on polysaccharide chemistry, polyoxypropylene-polyoxyethylene block co-polymers, and combination thereof, biodegradable ethoxylated alcohol sulfates, ethoxylated alkylphenol sulfates and sulfonates, and mixtures thereof, alkylarylpolyether of the type octylphenoxy-polyethoxyethanol, nonylphenylether polyethoxylates, amphoteric surfactants of the type alkylated carboxyalkyl, tertiary amines represented by the formula $R-N(CH_2CH_2COOx)_y$, where $x=H$, and $y=a$ member selected from the group consisting of Na, K, $(CH_3)_4N^+$ (tetramethylammonium radical), and betaine derivatives.
2. The aqueous cleaning composition of claim 1, wherein said salt of hydroxy carboxylic acid is a salt of an α -hydroxy carboxylic acid.
3. The aqueous cleaning composition of claim 2, wherein said α -hydroxy carboxylic acid is a member selected from the group consisting of lactic acid, aspartic acid, citric acid, tartaric acid, mandelic acid, gluconic acid, glycolic acid and combination thereof.
4. The aqueous cleaning composition of claim 2, wherein said salt is a member selected from the group consisting of, sodium lactate, potassium lactate, sodium aspartate, potassium aspartate, sodium citrate, potassium citrate, sodium tartrate, potassium tartrate, sodium gluconate, potassium gluconate, and combinations thereof.
5. The aqueous cleaning composition of claim 2, wherein said salt is selected from the group consisting of, tetramethylammonium lactate (TMA-lactate), TMA-aspartate, TMA-citrate, TMA-tartrate, TMA-gluconate and combinations thereof.
6. The aqueous cleaning composition of claim 2, wherein said salt is derived from the neutralization reaction of said hydroxycarboxylic acid with tetraethylammonium hydroxide, 2-hydroxyethyl-trimethylammonium hydroxide, and mixtures thereof.

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7. The aqueous cleaning composition of claim 1, wherein the composition comprises an organic base and the organic base is selected from the group consisting of aqueous quaternary ammonium hydroxides, the composition have a pH of at least about 12.1 and at most about 12.5.
8. The aqueous cleaning composition of claim 7, wherein said quaternary ammonium hydroxide is selected from the group consisting of tetramethylammonium hydroxide (TMAH), tetraethylammonium hydroxide, 2-hydroxyethyl-trimethylammonium hydroxide, and mixtures thereof.
9. The aqueous cleaning composition of claim 1, wherein the composition comprises an inorganic base and the inorganic base is selected from the group consisting of alkali metal carbonate, bicarbonate, hydroxide, sesquicarbonate and combinations thereof.
10. The aqueous cleaning composition of claim 9, wherein said alkali metal is selected from a group consisting of Na, K, and combination thereof.
11. The aqueous cleaning composition of claim 1, further comprising a surface active agent selected from the group consisting of non-ionic surfactants, ionic surfactants, amphoteric surfactants and combinations thereof.
12. The aqueous cleaning composition of claim 1, wherein total concentration of active ingredients in said cleaning solution consists of hydroxycarboxylate salt, and excess base is in the range between about 0.5 to about 5 percent.
13. The aqueous cleaning composition of claim 12, wherein the total concentration of active ingredients is in the range between about 0.8 and 2.5 percent in water (wt/vol).
14. The aqueous cleaning composition of claim 1, wherein the base is inorganic and the pH of the solution is in the range of between about 11.5 and about 12.8.
15. The aqueous cleaning composition of claim 14, wherein the pH of the solution is in the range of between about 12.0 and about 12.4.
16. The aqueous cleaning composition of claim 1, wherein the at least one surfactant is present between about 0.01 and about 0.5 wt %.
17. The aqueous cleaning composition of claim 16, wherein at least one surfactant is present between about 0.02 and about 0.3 wt %.

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(12) United States Patent

Sachdev et al.

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(54) AQUEOUS QUATERNARY AMMONIUM HYDROXIDE AS A SCREENING MASK CLEANER

(75) Inventors: Krishna G. Sachdev; John T. Butler, both of Hopewell Junction; Michael E. Cropp, LaGrangeville; Donald W. DiAngelo, Fishkill; John F. Harmsuth, Pleasant Valley; James N. Humenik, LaGrangeville; John U. Knickerbocker, Hopewell Junction; Daniel S. Macklin, Pleasant Valley; Glenn A. Pomerantz, Kerhonkson, all of NY (US); David E. Speed, Newtown, CT (US); Candace A. Sullivan, Pleasant Valley, NY (US); Bruce E. Tripp, Rhinebeck, NY (US); James C. Utter, Fishkill, NY (US)

(73) Assignee: International Business Machines Corporation, Armonk, NY (US)

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(52) U.S. Cl. 134/2; 134/38

(58) Field of Search 134/34, 2, 1, 1.3, 134/38; 510/175

(56) References Cited

U.S. PATENT DOCUMENTS

4,068,994 * 1/1978 Cadwallader et al. 425/110
4,245,273 1/1981 Feinberg et al.
4,483,040 11/1984 Magee et al.
4,592,856 6/1986 Kobayashi et al.
4,964,919 10/1990 Payne
5,091,103 2/1992 Dean et al.
5,188,986 2/1993 Liu et al.
5,304,252 * 4/1994 Condra et al. 134/2

5,350,489 9/1994 Murakami
5,407,788 4/1995 Fang
5,466,389 11/1995 Hardi et al.
5,472,513 12/1995 Shiramizu
5,498,293 3/1996 Hardi et al.
5,529,887 * 6/1996 Horn et al. 430/331
5,545,309 8/1996 Shimizu et al.
5,563,119 10/1996 Ward
5,704,987 * 1/1998 Huyah et al. 134/6
5,780,406 * 7/1998 Honda et al. 510/175
5,858,118 * 1/1999 Shah et al. 134/29
5,888,308 * 3/1999 Sachdev et al. 134/2
5,904,156 * 5/1999 Advocate, Jr. et al. 134/2

FOREIGN PATENT DOCUMENTS

408269495 A * 10/1996 (JP).

OTHER PUBLICATIONS

"A Fabrication Technique for Multilayer Ceramic Modules" by H. D. Kaiser, F. J. Pakulski and A. F. Schmeckenbecher. IBM Components Division, East Fishkill Facility; Hopewell Junction, New York. Solid State Technology/May 1972; pp. 35-40.

* cited by examiner

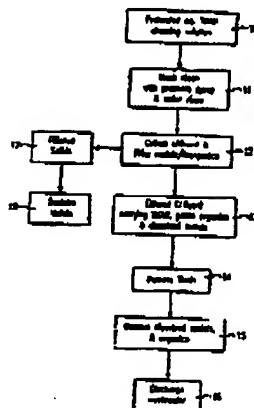
Primary Examiner—Randy Gulakowski

Assistant Examiner—Saeed Chaudhry

(57) ABSTRACT

This invention relates to the cleaning of objects that relate to semiconductor printing, such as, for example, screening masks. This invention is basically directed to removing, for example, an organic polymer-metal composite paste from screening masks used in printing conductive metal patterns onto ceramic green sheets in the fabrication of semiconductor packaging substrates. More particularly, this invention is concerned with the automated in-line cleaning of paste screening masks with an aqueous alkaline solution of a quaternary ammonium hydroxide as a more environmentally friendly alternative to non-aqueous organic solvents-based cleaning in screening operations for the production multilayer ceramic (MLC) substrates.

26 Claims, 4 Drawing Sheets



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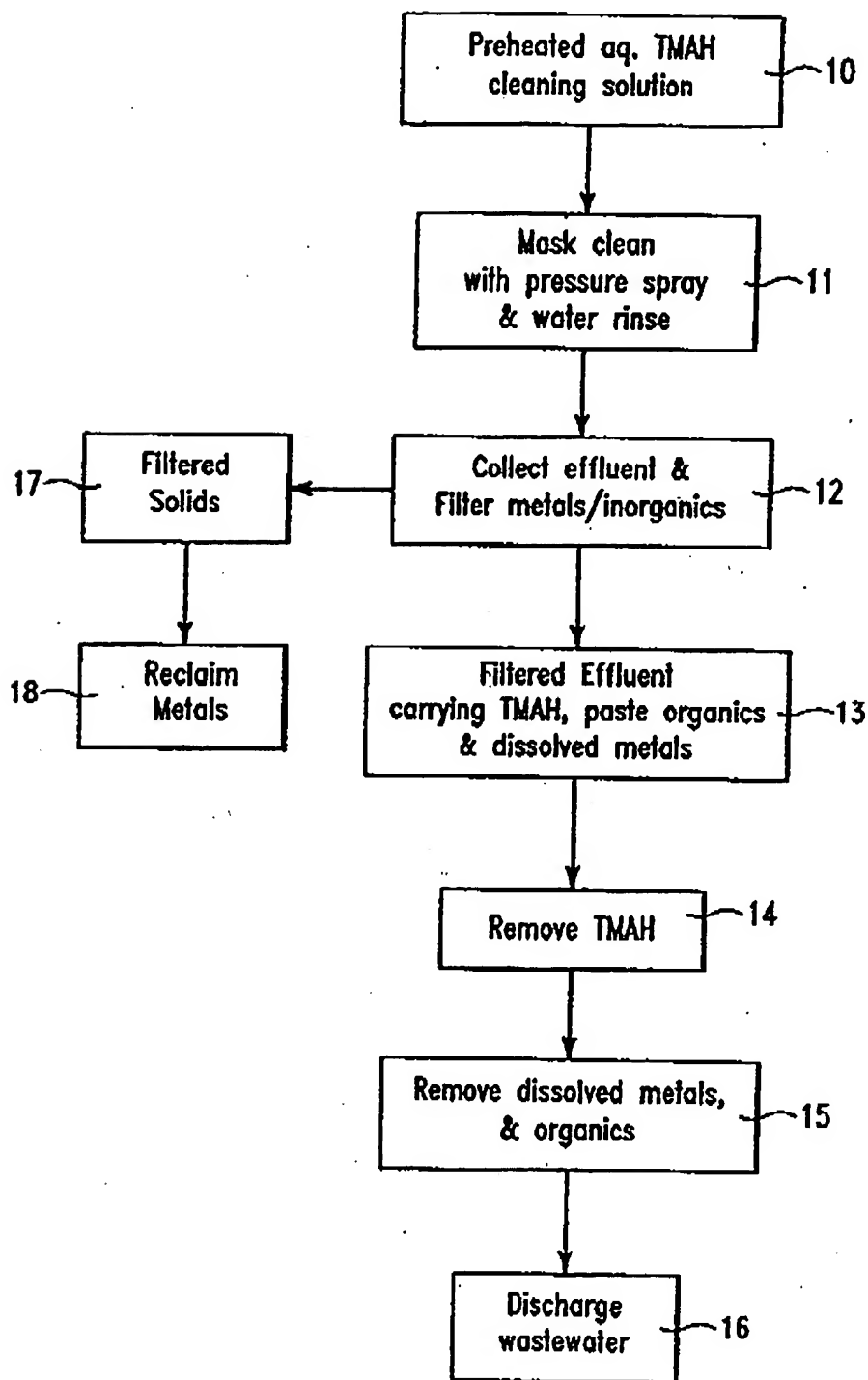


FIG. 1

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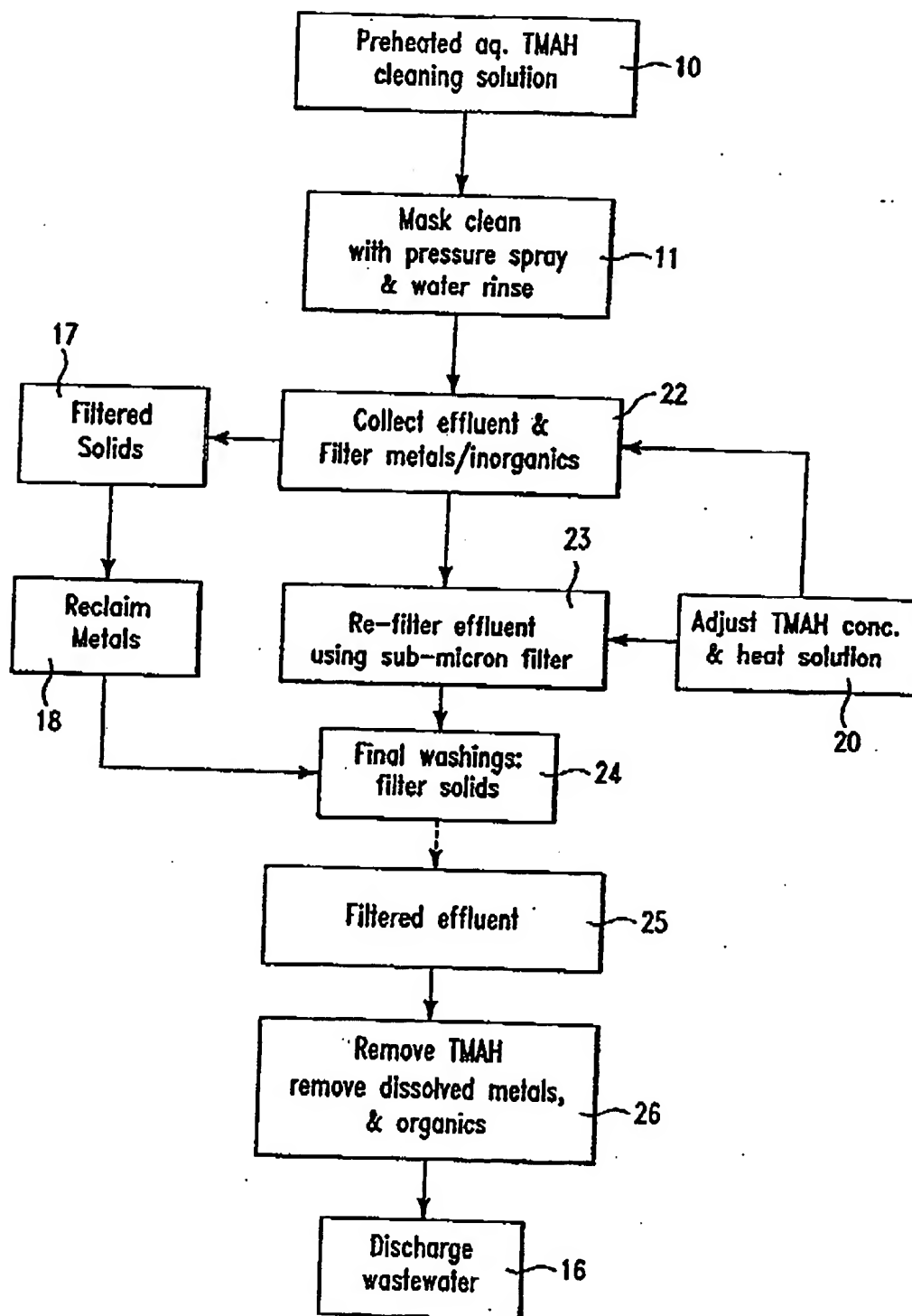


FIG. 2

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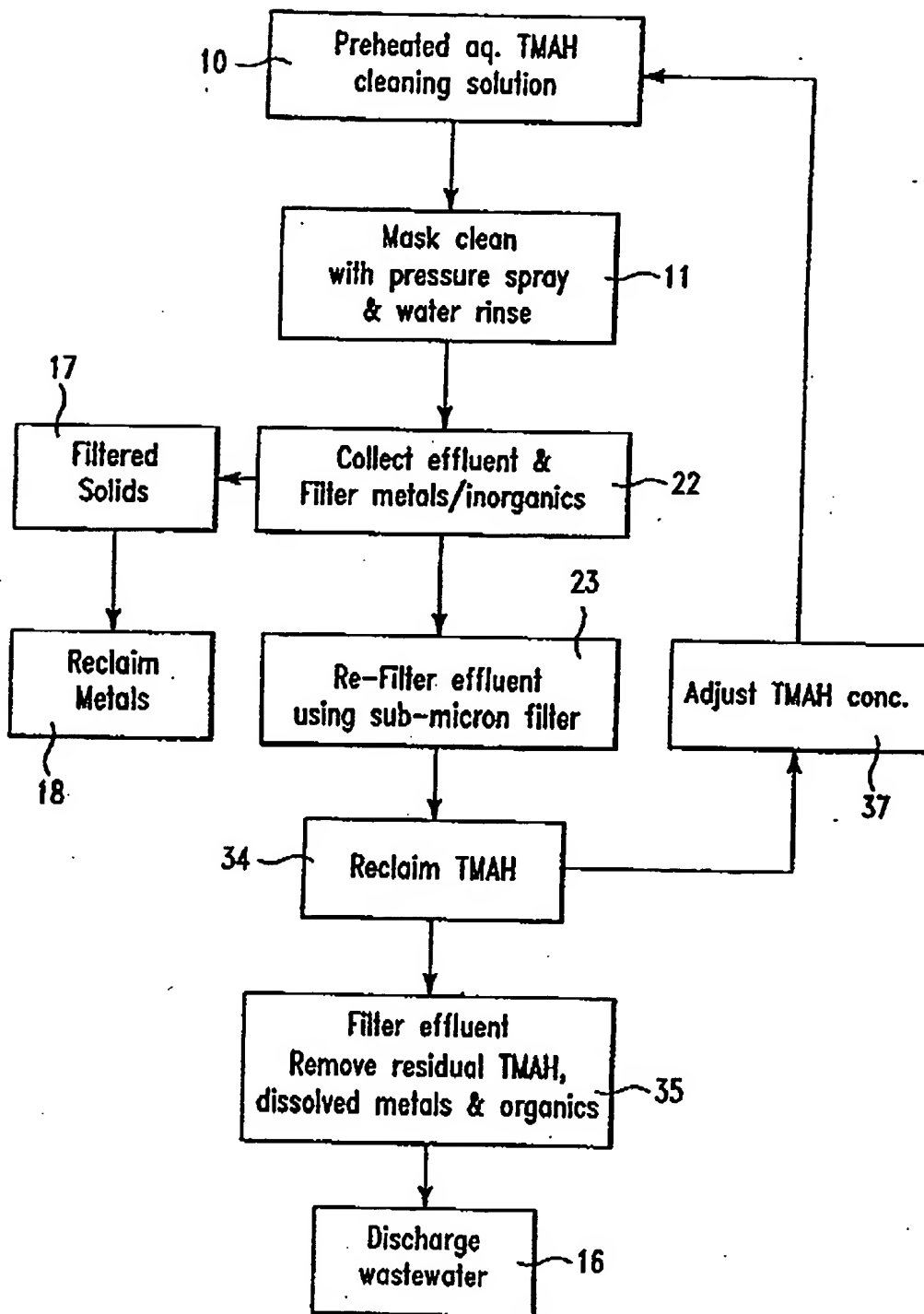


FIG. 3

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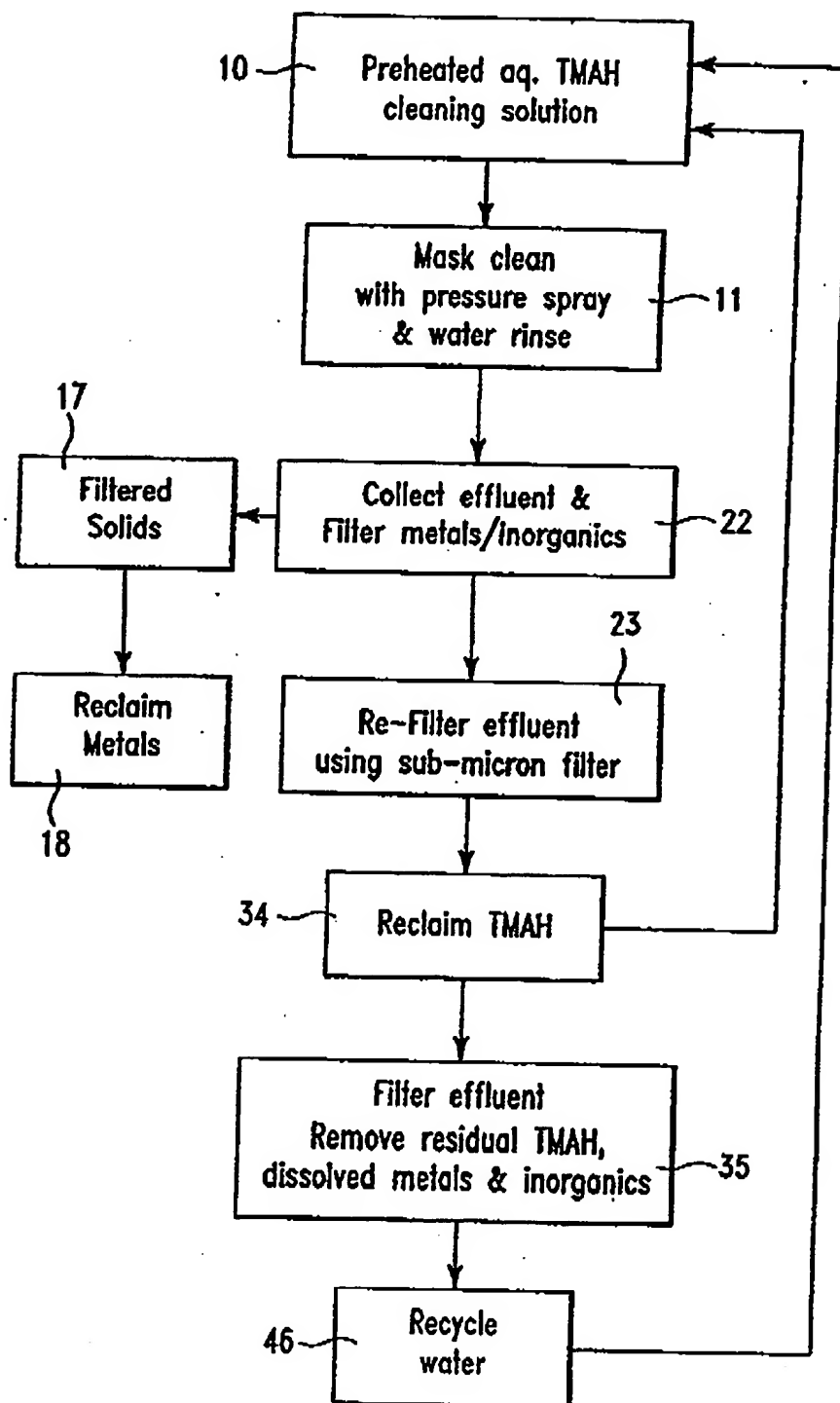


FIG. 4

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AQUEOUS QUATERNARY AMMONIUM HYDROXIDE AS A SCREENING MASK CLEANER

FIELD OF THE INVENTION

This invention relates to cleaning of objects that relate to semiconductor printing, such as, for example, screening masks. This invention is basically directed to removing, for example, an organic polymer-metal composite paste from screening masks used in printing conductive metal pattern onto ceramic green sheet in the fabrication of semiconductor packaging substrates. More particularly, this invention is concerned with automated in-line cleaning of paste screening masks with aqueous alkaline solution of a quaternary ammonium hydroxide as an environmentally friendly alternative to non-aqueous organic solvents based cleaning in screening operations for the production multilayer ceramic (MLC) substrates.

BACKGROUND OF THE INVENTION

In the fabrication of multilayer ceramic substrates for packaging semiconductor devices, conductive metal patterns are screened on individual ceramic green sheets by printing, such as, extrusion printing, using mask, such as, a metal mask, placed in contact with the green sheet. The screen printing method involves squeezing paste onto the green sheet surface using a mesh mask or an emulsion mask. After screening, the green sheets are assembled and aligned, and laminated followed by a sintering operation to form a multilayer ceramic substrate. Fabrication techniques for such substrates, including design, screening equipment, and paste screening process are well known in the art.

However, advance ground rule electronic packaging requires printing closely spaced conductive metal pattern on a substrate, and using a screening mask that has highly dense fine dimension etched features. It has been observed that such screening masks have the problem of paste residue entrapment in the mask features in addition to a surface residue when the paste is screened to deposit conductive pattern onto the green sheets. This requires that the metal mask be cleaned after one or more screening passes to eliminate/minimize the possibility of defects in subsequently screened pattern. Any defects in the screened paste pattern replicates into the final product causing yield losses. On the other hand, mesh masks can be used for multiple screening passes, typically 100-200 green sheets may be screened using the same mesh mask before it requires cleaning and therefore, the cleaning frequency for a mesh mask is relatively low in comparison to a metal mask.

Conductive pastes used in screening processes for the delineation of wiring, vias, I/O (input-output) pads, and other pattern features comprise metal particles with or without added inorganic particulate fillers. These constituents are mixed with an organic binder and solvent vehicle along with wetting agents, dispersants/surfactants, plasticizers, and other additives such as thickening agents, antioxidants, and coloring agents which are well known in the fabrication of electronic components.

Most commonly used conductive pastes in multilayer ceramic fabrication are based on molybdenum or tungsten metal powders dispersed in an organic polymer binder, such as, for example, ethyl cellulose, polymethylmethacrylate, and the like, or polyhydrocarbon based thermoplastic resins in a high boiling solvent vehicle.

Other conductive pastes that can be used for screening processes in multilayer ceramics could comprise copper,

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gold, nickel, tin, to name a few. Because of the variety and complex chemical make-up of polymer-metal pastes, it is required that the mask cleaning medium and process selected be such that it provides complete and efficient cleaning of all types of pastes from screening masks and associated equipment.

In automated processes for high volume production of multilayer ceramic substrates, it is also necessary that the speed of mask cleaning be compatible with the cycle time pre-set by the throughput requirement and other dependent operations.

Recently, several water-based cleaners have become commercially available and many aqueous detergent compositions have been described for cleaning/degreasing purposes, for example, printed circuit board assemblies and other parts in device fabrication to remove soldering flux, oil/grease, and other organic residues invariably formed during bonding and assembly processes in microelectronics. These are generally based on a combination of surfactants in water and/or alkaline detergent compositions comprising alkali metal salts, such as, sodium metasilicate, sodium carbonate, tribasic sodium phosphate, sodium tripolyphosphate, and combinations thereof, as well as highly alkaline solutions based on alkali metal salts, alkali metal hydroxides, and mixtures thereof with alkanolamines. Aqueous cleaner formulations comprising this category of alkaline detergents are described in U.S. Pat. No. 5,234,506 (Winston) and U.S. Pat. No. 5,264,047 (Winston) for removing soldering flux, wax, and grease from printed circuit boards.

One of the major considerations with aqueous cleaning is wastewater management for compliance with the Clean Water Act regulations, which requires that all possible sources of aquatic impact and other environmentally undesirable constituents be removed from the effluent before discharge to surface waters. This requires special and costly wastewater treatments, such as, precipitation with complexing agents to form sludge that carries active ingredients of cleaning compositions, metals, and other dissolved constituents, and which results in solids loading to the waste. To minimize waste and reduce cost with conservation of water in aqueous cleaning, there is currently significant industry direction toward environmentally suitable zero waste processes by devising a methodology for reclamation, recycling, reuse, etc.

U.S. patent application Ser. No. 09/096,840, filed on Jun. 12, 1998, entitled "REMOVAL OF SCREENING PASTE RESIDUE WITH QUATERNARY AMMONIUM HYDROXIDE-BASED AQUEOUS CLEANING COMPOSITIONS", assigned to the assignee of the instant patent application, and the disclosure of which is incorporated herein by reference, discloses the use of quaternary ammonium hydroxide-based aqueous cleaning compositions as a more environmentally friendly medium for removing screening paste residue.

PURPOSES AND SUMMARY OF THE INVENTION

The invention is a novel method of cleaning paste from screening masks using at least one aqueous quaternary ammonium hydroxide as a cleaner.

Therefore, it is a purpose of this invention to provide a water-based cleaning method for cleaning paste residue from screening masks used in the manufacturing of multilayer ceramic substrates.

Another purpose of this invention is to provide an aqueous cleaning method for automated in-line cleaning of

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screening masks, in multi-layer ceramic manufacturing in high volume production.

Yet another purpose of this invention is to provide aqueous cleaning method for paste cleaning from screening masks, by using water-based solution of a quaternary ammonium hydroxide to eliminate volatile emissions and hazardous wastes associated with non-aqueous solvent based cleaning processes.

Still yet another purpose of this invention is to provide method for in-line mask cleaning with aqueous alkaline solution comprising a quaternary ammonium hydroxide as a single active ingredient which can be recovered and recycled.

Still another purpose of this invention is to provide aqueous alternative to organic solvents in mask cleaning by using an aqueous alkaline solution containing tetramethyl ammonium hydroxide that is effective in removing polar, non-polar, or hydrophilic and hydrophobic paste residue from metal and polymer surfaces.

It is also a purpose of this invention to provide an aqueous cleaning method for screening masks which does not require special wastewater treatment.

Yet another purpose of this invention is to provide an aqueous cleaning method for paste screening masks which provides an option for metals recovery from the effluent and minimizes waste in multilayer ceramic production.

Still another purpose of this invention is to provide an aqueous cleaning method using quaternary ammonium hydroxide containing compositions which are compatible with metal masks, emulsion masks, polymer adhesives used in mask assembly, and all contacting materials in cleaning tools associated with paste making equipment.

Still yet another purpose of this invention is to provide a cleaning method with an aqueous alkaline solution which is free of foaming problems when used under high pressure spray conditions.

Therefore, in one aspect this invention comprises an aqueous cleaning method for cleaning paste residue from at least one screening object comprising the use of at least one aqueous alkaline solution containing at least one quaternary ammonium hydroxide.

In another aspect this invention comprises a cleaning apparatus comprising:

- (a) at least one means for pressurized spray cleaning of at least one screening object carrying screening paste residue with at least one solution; and
- (b) wherein said at least one solution comprises at least one aqueous alkaline composition having at least one quaternary ammonium hydroxide.

BRIEF DESCRIPTION OF THE DRAWINGS

The features of the invention believed to be novel and the elements characteristic of the invention are set forth with particularity in the appended claims. The drawings are for illustration purposes only and are not drawn to scale. Furthermore, like numbers represent like features in the drawings. The invention itself, however, both as to organization and method of operation, may best be understood by reference to the detailed description which follows taken in conjunction with the accompanying drawings in which:

FIG. 1, illustrates a process flow chart for an embodiment of this invention using an aqueous tetramethyl ammonium hydroxide (TMAH) for cleaning a screening mask.

FIG. 2, illustrates a process flow chart for another embodiment of this invention where the effluent from the aqueous TMAH used for cleaning a screening mask is reused.

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FIG. 3, illustrates a process flow chart for yet another embodiment of this invention where the TMAH used for cleaning a screening mask is reclaimed and reused.

FIG. 4, illustrates a process flow chart for still another embodiment of this invention where the TMAH and the water used for cleaning a screening mask is reused or recycled.

DETAILED DESCRIPTION OF THE INVENTION

This invention is basically concerned with a method of removing screening paste residue from screening masks and ancillary equipment used in screening conductive paste patterns on ceramic green sheet in the manufacture of multilayer ceramic substrates. This invention is particularly concerned with removing polymer-metal composite paste residue from screening masks in high throughput multi-layer ceramic production using an aqueous solution of a metal-ion-free organic base, specifically tetramethyl ammonium hydroxide (TMAH) and related organic quaternary ammonium hydroxides to provide a more environmentally friendly alternative to non-aqueous organic solvents cleaning processes.

Unless specified otherwise, the percentages given are in vol % (volume percent) and in wt % (weight percent).

The aqueous cleaning method according to this invention is environmentally friendly, and provides an option for the recovery of precious metals from the solid waste in the effluent. Aqueous cleaning with tetramethyl ammonium hydroxide according to this invention provides unique advantages of compatibility with recovery and recycling of the TMAH (tetramethyl ammonium hydroxide) and other quaternary ammonium hydroxides, reclamation of metals, and not requiring use of any surfactants or other additives, or alkali-metal silicates and/or phosphates.

The manufacturing of semiconductor packaging products, such as multilayer ceramic substrates, typically employs the technique of conductive pattern screening on a ceramic green sheet through a stencil mask using a variety of polymer-metal composite pastes to delineate conductive pattern for the desired circuitry. In this process, some paste residue is left behind on the surface and inside the fine etched features of the mask. The residue entrapped in the mask features and on the surface of the mask must be removed if the mask is to be reused for paste screening. Using automated screening and mask cleaning processes, mask cleaning may be done after one or more screening passes depending on whether the paste is fast drying or slow drying, otherwise the paste residue on the mask can cause defects in subsequently screened conductive patterns. Particular combinations of polar and/or non-polar polymer binders and solvent vehicle systems, which are selected for dispersing metal powders, determines the solubility and wettability characteristics of the resulting paste, which may range from hydrophilic to highly hydrophobic, and which may be fast drying or slow drying.

Selection of conductive screening pastes that are based on a variety of polymer binder-solvent vehicle systems is dictated by several considerations, viz, the requirement for a particular circuit pattern, drying characteristics of the paste, the shrinkage match of the paste with that of the ceramic, and the overall compatibility of the paste with the green sheet materials for the necessary wettability and adhesion.

Screening masks are typically made of metal, such as, etched Mo masks, electroform masks and emulsion masks

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for silk screening, such as, for example, a stainless steel mesh with at least one photoresist coating of a suitable emulsion such as a polyacrylic-polyester based emulsion coating.

As stated earlier, in the high volume production of multilayer ceramic substrates, an in-line screening and mask cleaning method using organic solvent pressurized spray is described in U.S. Pat. No. 4,483,040 (Magee), the disclosure of which is incorporated herein by reference.

The present invention provides a cleaning method for mask cleaning with aqueous quaternary ammonium hydroxide solution, specifically tetramethyl ammonium hydroxide (TMAH) and related quaternary ammonium hydroxides as an environmentally friendly alternative to non-aqueous organic solvents for the effective cleaning of polymer-metal composite paste residue in multilayer ceramic manufacturing.

Aqueous tetramethyl ammonium hydroxide (TMAH) is widely used in the semiconductor industry as a metal-ion-free resist developer in lithographic processes for integrated circuit device fabrication. Semi-aqueous cleaning compositions containing TMAH for the removal of baked photoresist residues, and for cleaning semiconductor wafers and wafer carriers have been known. For example, U.S. Pat. No. 5,407,788 (Fang) describes the use of TMAH in non-aqueous solvent for stripping cured negative resist patterns; U.S. Pat. No. 5,350,489 (Muraoka) teaches the use of quaternary ammonium hydroxide solutions for cleaning plastic molded items used in chemical analysis and wafer carriers to remove impurities of fine particles and fats and oils; U.S. Pat. No. 5,466,389 (Iardi); and U.S. Pat. No. 4,964,919 (Payne) are concerned with cleaning silicon wafers using cleaning compositions at 8-10 pH comprising quaternary ammonium hydroxide related organic bases or alkali metal hydroxides in combination with surfactants and buffering agents, such as, acetic acid, ammonium chloride, and ammonium acetate, for adjusting pH to less than 10; U.S. Pat. No. 4,592,856 (Kobayashi) discloses the removal of oil/grease and resinous contaminants from the surface of plastic articles and molding equipment for eye glass lenses and optical instruments using detergent compositions comprising TMAH or 2-hydroxyethyl trimethyl ammonium hydroxide (Choline) in chlorinated solvents as perchloroethylene, 1,1,1-trichloroethane, methylene chloride, an ionic/non-ionic surfactant and methyl alcohol.

As stated earlier, the primary purpose of the present invention is to employ an aqueous-based cleaning alternative to organic solvents in automated mask cleaning to remove conductive screening paste residue. These pastes are used for defining via and wiring metallurgy patterns on ceramic green sheets and are comprised of a metal constituent, such as, molybdenum, copper, tungsten, nickel, gold, palladium, platinum and silver, some of which may also contain inorganic fillers, such as, glass, ceramic powder, or glass frit, dispersed in an organic polymer binder and a high boiling organic solvent vehicle along with other necessary additives which include surfactants/dispersants, coloring agents, thickening agents or viscosity modifiers, and antioxidants etc.

The invention may also be used to clean masks and screens which are used in the application of solder pastes to various microelectronics components.

Representative polymer binder systems in conductive paste formulations for multilayer ceramics include: cellulose polymers, such as, ethylcellulose, acrylate polymers, such as, polymethylmethacrylate, polyhydrocarbon based

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thermoplastic resins which are all hydrophobic, or the binder can be hydrophilic such as hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxymethyl cellulose, and the like.

The preferred high boiling solvent, vehicles having a low evaporation rate in paste dispersions include ester-alcohol or glycol ether type solvents such as 2,2,4-trimethylpentane diol, 1,3, monoisobutylate (Texanol), diethylene glycol monomethylether acetate, diethylene glycol monobutylether acetate or butyl carbitol acetate (BCA), and the like. Generally, the solid component in screenable pastes comprises 60 to 85 percent (wt. %) metal constituent, 1 to 5 percent of organic polymer binder and other organic and inorganic additives, and the balance constituting the solvent vehicle system.

Depending on a particular binder-solvent vehicle system used in the paste formulation, the paste can be polar or non-polar, hydrophilic or oleophilic, have differences in affinity and adhesive characteristics for the mask surface, in addition to having differences in the drying rate.

According to this invention, it has been found that paste residue left on screening masks, in the process of conductive pattern screening on green sheet, is readily removed by pressure spray cleaning, with a dilute solution of tetramethyl ammonium hydroxide (TMAH) and/or related quaternary ammonium hydroxides. It was also found that pressure spray cleaning of masks with a heated dilute solution of TMAH provides reduction in cycle time. It was further found that mask cleaning using a high pressure spray of heated TMAH required a reduced concentration of TMAH and also provided a cycle time reduction. In mask cleaning with aqueous TMAH using a pressurized spray method, it is found that the minimum pH of aqueous TMAH solution must be at least above 11.5, preferably between about 11.8 and about 13.1, for it to be effective in the complete removal of the paste residue from the masks.

In one embodiment of this invention, Mo metal masks carrying conductive paste residue from a screening pass are spray cleaned with an aqueous TMAH $[(CH_3)_4N^+OH^-]$ solution comprising less than 1.0 wt. % TMAH dissolved in water, for about 30 to about 45 sec by using a hand-held spray nozzle or with a multi-nozzle spray at between about 50 and about 70 psi and between about 130° F. to about 150° F. solution temperature.

Subsequent to washing with TMAH, the screened masks are immediately rinsed with water and dried, preferably with forced hot air or nitrogen. In another embodiment of this invention, masks can be cleaned in less than about 15 sec to about 20 sec with less than about 1 wt % TMAH $[(CH_3)_4N^+OH^-]$ in water, using a high pressure spray wash employing a specially designed multi-nozzle system at between about 150 and about 200 psi and between about 130° F. and about 180° F. in an automated in-line paste screening and mask cleaning machine, such as, described in U.S. Pat. No. 4,483,040, and/or U.S. patent application Ser. No. 09/021, 046, (Casey) filed on Feb. 9, 1998, entitled "OPTIMIZED IN-LINE MASK CLEANING SYSTEM", the disclosure of which are incorporated herein by reference. High pressure spray wash under these conditions is especially preferred for automated screening and mask cleaning operations for the high volume production of multilayer ceramic substrates.

The cleaning tool employs a specially designed multi-nozzle spray head having top to bottom angled sets of nozzles that direct the spray on both sides of the mask simultaneously while sweeping across the mask in a pre-set time cycle. With this type of in-line mask cleaning machine,

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the cleaning process with aqueous TMAH typically involves a high pressure spray cleaning at between about 100 and about 185 psi at between about 130 and about 180° F. for between about 10 and about 20 sec followed by a pressure spray rinse with water at between about 60 and about 70 psi in the same chamber or in a separate chamber and then drying with an air knife or blow drying with nitrogen.

It was also found that high pressure spray cleaning at between about 170 and about 190 psi with a heated aqueous TMAH solution at a concentration, as low as about 0.3 wt %, also provides effective cleaning of various types of paste residues accompanied by longer wash times, followed by the usual water spray rinse and hot air or nitrogen drying.

Spray cleaning with aqueous TMAH as disclosed herein effectively and efficiently removes all types of paste residues that may include polar, non-polar, hydrophilic, and hydrophobic types of pastes from stencil masks, typically Mo metal, electroform masks, and emulsion masks.

Tetramethyl ammonium hydroxide (TMAH) is the preferred organic base for mask cleaning applications according to this invention but other related commonly known quaternary ammonium hydroxides that may also be used are: tetrabutyl ammonium hydroxide, tetrabutyl ammonium hydroxide, trimethyl-2-hydroxyethyl ammonium hydroxide (Choline), triethyl-2-hydroxy ethyl ammonium hydroxide, ethyltrimethyl ammonium hydroxide, and the like.

The aqueous alkaline cleaning solution comprising quaternary ammonium hydroxides may optionally contain one or more corrosion inhibitor.

According to a preferred embodiment of this invention, a pressurized spray wash at between about 50 to about 200 psi with a heated aqueous solution of tetramethyl ammonium hydroxide (TMAH) containing between about 0.3 and about 2.0 wt % TMAH based on $(CH_3)_4N^+OH^-$ provided a highly effective cleaning of masks.

However, a high pressure spray at between about 100 psi and about 180 psi with a heated solution was preferred for the automated cleaning of stencil masks to remove conductive paste residue. This automated cleaning would provide a highly efficient process suitable for high volume production environment.

The overall cleaning process involves a pressure spray clean with aqueous TMAH which is immediately followed by a water spray rinse, and air or nitrogen drying operations to provide clean masks ready for use in the next screening and cleaning cycle. The volume of cleaning solution and water rinse per cycle per mask in the pressurized spray depends on the type of spray nozzles, the spray time, and the spray pressure. To accelerate the drying of masks after the water rinse cycle, the masks may be spray rinsed with a lower boiling solvent as isopropyl alcohol or simply exposed to its vapor and then air or nitrogen blow dried. The cycle time for cleaning can be further reduced by increasing the TMAH concentration, but this is not preferred due to a high pH concn, increased cost of cleaning and TMAH removal from the effluent before waste water discharge.

The effluent from the cleaning process described herein contains soluble and insoluble paste constituents and most of the original dissolved TMAH. It has been found that the metal and inorganic solids in the wash separate out in a form which can be readily removed by filtration. The filtered effluent after solids removal contains TMAH and dissolved organics of the paste residue removed from the masks.

FIG. 1, illustrates a process flow chart for an embodiment of this invention using an aqueous TMAH for cleaning a screening mask. The TMAH cleaning solution made accord-

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ing to this invention is preferably pre-heated at step 10. The heated solution of step 10, is then used to clean a mask or any related equipment at step 11. This cleaning at step 11, can be done either manually or automatically. One could use a single or a multi-nozzle cleaning spray to do the cleaning of the screening parts. After the cleaning process it is preferred that the cleaned parts are rinsed with water and then dried to remove any surface water or moisture. The effluent from the cleaning process of step 11, is collected and filtered at step 12. At step 13, the filtered effluent from step 12, which contains dissolved, soluble TMAH, paste organics and any dissolved metals, etc. is collected. At step 14, one would remove the TMAH, from the filtered effluent of step 13. The dissolved metals and organics in the TMAH-free effluent after step 14, could be removed at step 15, leaving wastewater which would be discharged at step 16. It is preferred that at step 12, the solids are filtered out as step 17, and that the metals if any are reclaimed at step 18. Basically, the effluent generated in the pressure spray wash with aqueous TMAH at step 11, is filtered at step 12, using a coarse filter, to remove solids, which include insoluble metals and inorganics, collected at step 17, and the filtered effluent is collected at step 13, which is followed by the removal of TMAH from the filtrate at step 14, for example, by ion-exchange resin. After the TMAH is removed at step 14, the wastewater can be further treated to remove any dissolved paste organics and soluble metals at step 15, for example, by passing through adsorbing media, activated charcoal, or lime treatment, following which wastewater can be safely discharged or reused at step 16. It is preferred that the filtered metal solids at step 17, are processed to reclaim precious metals, if any, at step 18. As shown in FIG. 1, the solids-free effluent can be further subjected to a process sequence for removing, TMAH, any dissolved metal, and organics, and to provide contaminant-free wastewater which may be safely discharged or reused.

FIG. 2, illustrates a process flow chart for another embodiment of this invention where the effluent from the aqueous TMAH used for cleaning a screening mask is reused at least once again before waste discharge. The filtered effluent after step 11, at step 22, would be collected and would be subjected to microfiltration at step 23, and reused at least once after adjustment of the TMAH concentration at step 20, to make up for the dilution caused by mixing with the rinse water. At step 20, it is preferred that the adjusted TMAH solution is heated close to the same temperature as the original TMAH solution used in step 10, to clean the parts with once-used solution at step 11. The waste washing after reuse are filtered at step 24, to separate solids which are processed to reclaim metals in step 18, while the filtered effluent is collected at step 25. At step 26, one would remove TMAH dissolved metals and organics, and the wastewater would be discharged at step 16. It is preferred that the recovered filtered effluent of step 23, is only re-used once to prevent any degrading effect on the cleaning process due to increased dissolved paste organics, however, if the degradation of the process is not critical then the filtered effluent of step 23, could easily be used a multiple number of times. This mode of practicing the invention provides a number of benefits, such as, reduction in waste, reduced water consumption, reduced material cost, etc.

FIG. 3, illustrates a process flow chart for yet another embodiment of this invention where the TMAH used for cleaning a screening mask is reclaimed and recycled. In this embodiment of the invention the filtered effluent at step 23, is subjected to a TMAH removal process at step 34, and the

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recovered TMAH is recycled back into step 10, for mask cleaning. However, it is preferred that the concentration of the recovered TMAH is adjusted at step 37, to make up the cleaning solution in step 10. The wastewater in this case may contain any of the remaining dissolved organics and/or soluble metals which can be removed by standard methods in step 35, for example, by passing through adsorbing media allowing the safe discharge of contaminant-free water in step 16.

Basically, as illustrated in FIG. 3, the filtrate after removing all solids from the effluent in step 22, is subjected to a process for recovery of TMAH in step 34. This TMAH recovery could be done, for example, by passing the TMAH solution through an ion exchange column to trap the TMAH followed by an elution step and the recovery of TMAH, and regeneration of the column for a repeat recovery cycle. Ion exchange methods for the removal and recovery of quaternary ammonium hydroxides are well known in the art, see for example, U.S. Pat. No. 5,545,309 (Shimizu), which is concerned with the processing of quaternary ammonium hydroxide-containing liquid waste and he describes a cation exchange method in conjunction with electrolysis to remove and purify TMAH from spent photoresist developer solutions. The TMAH recovery method of this invention also involves a TMAH absorbing step and an eluting step followed by processing the eluate to recover an aqueous solution of TMAH. The reclaimed TMAH may be recycled which reduces material cost and eliminates waste. Removal of the metals and the TMAH from the effluent, reclamation and recycling especially of TMAH according to the mask cleaning method disclosed herein using aqueous TMAH offers a major benefit in terms of minimizing waste, lowering costs, and the safe discharge of wastewater. In addition to TMAH recovery and recycling, the wastewater may be subjected to additional purification and also recycled in the cleaning process, thus providing a close-loop system, as more clearly discussed in FIG. 4. This mode of practicing the invention has the benefit of further reducing waste and reducing material and process cost.

FIG. 4, illustrates a process flow chart for still another embodiment of this invention where the TMAH and the water used for cleaning a screening mask is reused. This embodiment of the invention essentially provides a close-loop mask cleaning method. According to this mode, both the TMAH at step 34, which is the active ingredient in cleaning, and water at step 46, are recovered and reused. The rest of the material recovery process is the same as discussed earlier.

The wastewater after removal of the TMAH in the present invention may contain residual dissolved organics from the washed-off paste, for example, cellulosic polymer, fatty acid esters, sarcosinate type dispersants, which are generally biodegradable.

The mask cleaning method using aqueous TMAH without additives also has several advantages over the multi-component aqueous alkaline solutions of the prior art comprising alkali metal silicates, phosphates, and surfactants. Specifically, such ingredients in the commonly known aqueous detergent compositions have environmental issues, require costly, waste-generating sludge forming wastewater treatment, and are not compatible with recovery from the effluent. These methods require the use of coagulants and flocculants, typically lime precipitation as Alum and iron salts, or PACs (polyaluminum chloride), organic polyelectrolytes etc, to precipitate silicates, phosphates, and other suspended matter from wastewater which adds solids to the waste. The 'sludge' or precipitated solids has associ-

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ated disposal issues of landfill limitation, disposal cost, and if there is any heavy metal contamination, it becomes a hazardous waste requiring a higher cost of waste disposal.

EXAMPLES

Various aspects of the present invention are further illustrated by referring to the following examples which are intended only to further illustrate the invention and are not intended to limit the scope of the invention in any manner.

Example 1

Molybdenum metal masks having fine pitch etched features for via and wiring metallurgical patterns, and for I/O pads, suitable for multi-layer ceramic substrates were used for screening conductive pastes onto ceramic green sheets with a paste screening tool. Various conductive pastes used for screening in ceramic technology generally comprise of a metal powder as the predominant component in a polymer binder-solvent vehicle matrix. Representative pastes screened onto green sheets using the metal masks contained between about 60 to about 85 percent metal powder, typically Molybdenum, Copper, Tungsten, and Nickel, in ethylcellulose type polymer binders, and high boiling polar solvents, for example, 2,2,4-trimethylpentane diol 1,3-monoisobutyrate, or diethylene glycol alkyl ether acetate in conjunction with fatty acid ester based surfactant, thickening agents, and other additives like antioxidants, coloring agents, corrosion inhibitors, etc.

Also tested were non-polar conductive pastes based on low molecular weight thermoplastic resins derived from petroleum hydrocarbons as the binder in place of cellulosic binders in combination with a hydrocarbon oil as the solvent vehicle.

Some of the pastes tested, in addition to carrying metal powder as the major component also contained inorganic fillers, such as, glass, ceramic, $Al_2O_3-SiO_2$ glass-frit. After the paste screening operation, the masks carrying the paste residue on surface and inside the etched features were cleaned with an aqueous tetramethyl ammonium hydroxide (TMAH) solution as described in the following sub-examples:

(a) Pressurized spray cleaning of paste residue on Mo masks using a single nozzle manual spray technique:

An aqueous tetramethyl ammonium hydroxide (TMAH) solution having about 1 wt % based on $(CH_3)_4N^+OH^-$ was prepared by diluting about 150 ml of about 25 wt % TMAH concentrate to about 1 gallon by adding deionized water. The solution was heated to between about 130 to about 150° F. and manually sprayed on to masks carrying paste residue at between about 50 to about 70 psi pressure with a single nozzle for between about 35 to about 45 seconds which removed paste residue from all areas of the masks. Immediately after TMAH spray clean, the masks were spray rinsed with water, preferably deionized water, for between about 20 to about 30 seconds and dried by blowing nitrogen or hot air. Microscopic inspection of the cleaned masks showed no evidence of paste residue in any area of the masks.

(b) Mask cleaning with aqueous TMAH according to the process of Example 1, but using less than 1 wt % TMAH:

Masks carrying screening paste residue were cleaned with an aqueous tetramethyl ammonium hydroxide (TMAH) solution having about 0.6 wt % based on $(CH_3)_4N^+OH^-$ prepared by diluting about 370 ml of about 25 wt % TMAH concentrate, to about 4 gallons with deionized water. The

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solution was heated to between about 150 to about 160° F., and manually sprayed on to masks carrying paste residue, at between about 50 to about 70 psi pressure, for between about 40 to about 50 seconds, followed by a water rinse using spray at between about 30 and about 40 psi for about 30 seconds, and drying by blowing hot air. Microscopic inspection of the cleaned masks showed no evidence of paste residue in any area of the masks.

Example 2

Automated high pressure spray cleaning of screening masks with aqueous tetramethyl ammonium hydroxide (TMAH):

About a 0.5 percent solution (wt % based on total solution volume) of TMAH was prepared by diluting one gallon of about 25 wt % aqueous $(CH_3)_4N^+OH^-$ concentrate with deionized water to form about 50 gallon of aqueous TMAH cleaning solution. The solution was pre-heated to between about 130° F. to about 150° F. with constant agitation in a heated reservoir with delivery pipes connected to the cleaning tool. Freshly screened Mo metal masks having paste residue from screening of Mo paste were transported to the cleaning chamber a few minutes after the screening pass, and subjected to a high pressure spray wash at about 150 to about 170 psi with the heated TMAH solution, using between about 12 to about 20 second automated wash cycle, followed by a water rinse cycle, and a hot air blow dry. Microscopic inspection of the cleaned masks showed complete removal of residue from all areas of the mask.

This was done for all paste types, i.e., polar type pastes comprising ethylcellulose-ethylene glycol alkyl ether acetate or ester-alcohol as the binder-solvent vehicle system, and the non-polar paste residue comprising hydrocarbon resin binder with non-polar oil as solvent vehicle.

Electroform masks having residue from screening of Cu, Mo and W pastes, when subjected to a similar cleaning procedure, showed complete removal of residue from all areas of the mask.

The following experimental results are representative of the cleaning effectiveness as a function of TMAH concentration, spray conditions, and wash cycle for a variety of pastes using an automated in-line screening and mask cleaning tool described in U.S. Pat. No. 4,483,040 (Magee) and U.S. patent application Ser. No. 09/021,046, (Casey), filed on Feb. 9, 1998, entitled "OPTIMIZED IN-LINE MASK CLEANING SYSTEM", the disclosures of which are incorporated herein by reference:

TMAH Conc. (percent)	Spray Pressure (psi)	Wash Cycle* (sec.)	Cleaning Results
0.2	180-185	17	marginal
0.2	185-190	12	poor
0.3	180-185	17	good
0.3	180-185	10	marginal
0.3	180-185	10	marginal
0.4	180-185	12	marginal
0.4	180-185	15	good
0.5	170-185	12	very good
0.5	100-120 psi/140° F.	12	good
2.0	150 psi/135° F.	17	very good
0.6	150 psi/135° F.	12	very good
0.6	120 psi/130° F.	12	very good

*In all cases, TMAH solution was pre-heated to between about 140° F. to about 170° F., unless indicated otherwise.

Example 3

Automated high pressure spray cleaning with aqueous tetramethyl ammonium hydroxide (TMAH) with effluent reuse:

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About 40 gallons of TMAH cleaning solution comprising about 0.5 wt. % of TMAH, was prepared by diluting about one gallon of about 25 wt % aqueous TMAH concentrate with about 49 gallons of deionized water. The solution was pre-heated to between about 160 to about 170° F. with constant agitation, in a reservoir with delivery pipes connected to the cleaning tool. Masks carrying screening paste residue were spray cleaned, water rinsed and dried according to the conditions described in Example 1. The wash and rinse from each mask was combined and filtered first through a 5-10 micron coarse filter to remove separated metal and inorganic solids, followed by microfiltration using about 0.2 micron cartridge filter. The filtered effluent was reconstituted to the original concentration of about 0.5 wt % TMAH by adding additional volume of the 25 wt % TMAH concentrate to make up for the dilution caused when the rinse water is combined with the wash, pre-heated and reused for cleaning another set of masks. Microscopic inspection of the cleaned masks showed no difference in the cleaning performance of the reconstituted effluent when compared with the masks cleaned according to Examples 1 and 2.

While the present invention has been particularly described, in conjunction with specific preferred embodiments, it is evident that many alternatives, modifications and variations will be apparent to those skilled in the art in light of the foregoing description. It is therefore contemplated that the appended claims will embrace any such alternatives, modifications and variations as falling within the true scope and spirit of the present invention.

What is claimed is:

1. An aqueous cleaning method for cleaning paste residue from at least one screening object comprising the use of an aqueous quaternary ammonium hydroxide alkaline solution consisting essentially of at least about 0.3% by weight and at most 2% by weight a member of the group consisting of quaternary ammonia hydroxides and mixtures thereof.

2. The method of claim 1, wherein said at least one quaternary ammonium hydroxide is selected from the group consisting of tetramethyl ammonium hydroxide, tetraethyl ammonium hydroxide, 2-hydroxyethyl trimethyl ammonium hydroxide (Choline), ethyltrimethyl ammonium hydroxide, tetrabutyl ammonium hydroxide, and mixtures thereof.

3. The method of claim 1, wherein said at least one aqueous alkaline solution containing at least one quaternary ammonium hydroxide further comprises 2-hydroxyethyl trimethyl ammonium hydroxide.

4. The method of claim 1, wherein said screening object is selected from the group consisting of a metal mask, an electroform mask, or an emulsion mask on a metal mesh.

5. The method of claim 1, wherein said paste residue comprises a metal and/or inorganic constituent with a polymeric binder, a solvent vehicle and a surfactant/dispersant, a thickening agent, and optionally at least one antioxidant, and/or at least one corrosion inhibitor.

6. The method of claim 1, wherein said at least one aqueous alkaline solution comprises aqueous tetramethyl ammonium hydroxide (TMAH).

7. The method of claim 6, wherein said aqueous TMAH solution comprises TMAH as an active ingredient based on $(CH_3)_4N^+OH^-$ in water at a concentration in the range of between about 0.3 wt % to about 2.0 wt %.

8. The method of claim 7, wherein said aqueous TMAH solution is used for cleaning according to a method comprising the steps of:

(a) heating said solution of claim 7, at between about 130 to about 190° F. with constant agitation,

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- (b) spraying said heated solution for between about 10 to about 20 seconds on said at least one screening object carrying at least one paste residue from at least one screening pass, using at least one high pressure spray wash, at a pressure of between about 70 to about 200 psi, with at least one multi-nozzle spray head, that sweeps across said object,
- (c) spray rinsing said object with hot water immediately following step (b) using said multi-nozzle spray head, at a pressure of between 50 to about 100 psi, for between about 10 to about 20 seconds, to remove any TMAH from said object.
9. The method of claim 8, wherein said object is dried with forced air or nitrogen.
10. The method of claim 8, wherein said tetramethyl ammonium hydroxide is removed from the effluent, reclaimed and recycled.
11. The method of claim 8, wherein the wastewater after removing TMAH from the effluent is purified and recycled to provide a close-loop aqueous cleaning method for screening objects.
12. The method of claim 8, wherein the effluent is microfiltered and reused before subjecting to TMAH removal operation.
13. The method of claim 6, wherein said aqueous TMAH solution comprises TMAH as an active ingredient based on $(\text{CH}_3)_4\text{N}^+\text{OH}^-$ in water at a concentration in the range of between about 0.3 wt % to about 1.0 wt %.
14. The method of claim 6, wherein said aqueous TMAH solution is used for mask cleaning by pressurized spray with at least one spray nozzle, at a pressure of between about 40 to about 200 psi, and at a temperature of between about 130 to about 190° F., for less than about 1 min.
15. The method of claim 6, wherein said aqueous TMAH solution is used for mask cleaning by a high pressure spray using at least one multi-nozzle spray system in an automated paste screening and mask cleaning machine.
16. The method of claim 15, wherein said cleaning solution contains less than about 1 wt % of TMAH in deionized water.

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17. The method of claim 1, wherein said cleaning paste comprises of at least one solder paste.
18. The method of claim 1, wherein said paste comprises of a metal constituent selected from a group consisting of molybdenum, copper, tungsten, nickel, gold, palladium, platinum and silver.
19. The method of claim 1, wherein said paste comprises of an inorganic filler selected from a group consisting of glass, ceramic powder and glass frit.
20. The method of claim 1, wherein said paste comprises an organic polymer binder and a high boiling organic solvent.
21. An aqueous cleaning method for cleaning paste residue from at least one screening object comprising the use of an aqueous quaternary ammonium hydroxide alkaline solution consisting essentially of at least about 0.3% by weight and at most 2% by weight of a member of the group consisting of tetramethyl ammonium hydroxide, triethyl ammonium hydroxide, 2-hydroxyethyl trimethyl ammonium hydroxide, ethyl-trimethyl ammonium hydroxide, tetrabutyl ammonium hydroxide and mixtures thereof.
22. The method of claim 21, wherein said quaternary ammonium hydroxide contains 2-hydroxyethyl trimethyl ammonium hydroxide.
23. The method of claim 21, wherein said at least one aqueous alkaline solution comprises aqueous tetramethyl ammonium hydroxide (TMAH).
24. The method of claim 23, wherein said aqueous TMAH solution comprises TMAH as an active ingredient based on $(\text{CH}_3)_4\text{N}^+\text{OH}^-$ in water.
25. The method of claim 23, wherein said aqueous TMAH solution comprises TMAH as an active ingredient based on $(\text{CH}_3)_4\text{N}^+\text{OH}^-$ in water at a concentration in the range of between about 0.3 wt % to about 1.0 wt %.
26. The method of claim 25, wherein said cleaning solution contains less than about 1 wt % of TMAH in deionized water.

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U. S. PATENT OFFICE

Metal Cleaning

SAMUEL SPRING, Ph.D.

*Technical Director
Oxford Chemical Corporation, Atlanta, Ga.*

*Formerly Laboratory Director
Kelite Corporation, Los Angeles, Calif.*

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CHAPTER

4

Special Methods of Cleaning

These include electrocleaning, steam cleaning, abrasive cleaning, and cleaning with ultrasonic energy. Steam cleaning is a general method used more in maintenance than in production cleaning, even though metal cleaning is involved. It does have application to production cleaning, however, and has more potential in this direction than is generally recognized. The subject order of Chapter 3 is used since this chapter is a continuation of methods of cleaning.

Electrocleaning

The part to be cleaned is made an electrode in a solution which can carry current through its ions. Upon passage of direct current, water is electrolyzed into hydrogen gas at the cathode and oxygen gas at the anode. The generation of gas in large volumes provides a high level of agitation, especially at those areas where the soil is partially removed. Here current can pass readily to or from the metal. In addition, the electrical charge imposed on the work is important in removing certain complex soils.

In the preparation of metal for electroplating, an electrocleaning stage is almost always used (Figure 19). Electrocleaning can also be used where high quality metal cleaning is to be carried out even if the metal is not to be electroplated. This is seldom done because of the expense of putting in direct current generators or rectifiers, whereas this type of equipment is available in electroplating establishments.

The work may be made either the cathode or the anode. If it is made the cathode, twice as much gas is generated as when it is the anode. On this basis, so-called direct current (cathodic cleaning) was used to a great extent at one time. However, it now appears that reverse current (anodic cleaning) is more desirable for most applications because there are fewer detrimental side effects.

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METAL CLEANING

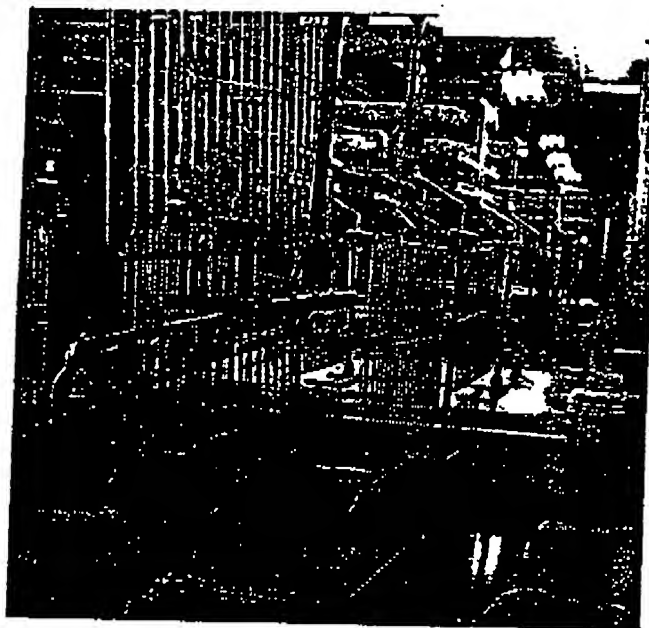


Figure 19. Wire racks for appliances are shown above being carried by the fully automatic plating conveyor at the Wire Division of Bauer Bros. Co., Springfield, Ohio. In the center of the photo may be seen a foam-blanketed tank containing 2500 gallons of electro-cleaner solution that is used in cleaning the wire racks prior to electroplating. (Courtesy Kelite Corp., Los Angeles)

Electrocleaning ordinarily follows other cleaning steps; in the preparation of metals for plating the metal usually goes into the electrocleaner in a reasonably clean condition except for traces of oily soil and modest quantities of finely divided solids and smut. Dirty work is also electrocleaned, often in two electrocleaning tanks to reduce contamination. In smaller establishments where the same cleaner is used for soak and electrocleaning, it is good practice to keep the parts in contact with the cleaner for perhaps two to three minutes before electrocleaning for one or two minutes. One reason is the avoidance of excessive electrocleaning which could cause detrimental electrode effects; another reason is to permit the soil to be removed sufficiently so as to expose a clean surface to serve as a center from which the gas bubbles can form and roll back the remainder of the soil. This demonstrates, moreover, that the alkaline electrocleaner must do more than supply ions to carry the current. The electrocleaner

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should have good detergency qualities to act on the soil while the so-called "scrubbing action" of the gas assists in soil removal. Surfactants are incorporated to provide detergency and a foam blanket.

A major function of the electrocleaner is to provide a foam blanket so that the spray of caustic solution entrapped by the gas bubbles, which are released at the electrodes, will be held at the surface of the cleaner long enough to permit the liquid to drain back into the bath. This reduces the release of corrosive fumes (see Chapter 5). Anyone who has been in a plating shop when the foam blanket on the electrocleaner is inadequate need not be reminded of the importance of this—there is coughing and sneezing on the part of everyone present.

Supplying the proper foam blanket for an electrocleaner is almost a fine art, particularly from the viewpoint of the compounder who must provide a single product appropriate to a broad variety of operating conditions. An ideal foam blanket consists of one to three inches of foam on the surface. It is interesting that the author, analyzing about 80 complaints against an electrocleaner (accumulated over a period of years), found that about half were for too much foam and half for too little foam. This situation is almost inevitable. The volume of gas generated varies from plant to plant while the presence of foam depressants or enhancers in the soil is unpredictable. Finely divided solids of the type found in smuts can stabilize foams which then build up to excessive amounts. Surfactants for electrocleaners normally yield foam of low stability. Where more foam is needed, surfactants may be added at the tank because the need may be occasional.

A problem with excessive foam in electrocleaning is that hydrogen and oxygen gas accumulated in the foam can explode at a sparking electrode. This is more a nuisance than menace in most cases, and is considered poor plant practice. Another difficulty is that foam dried onto the work may be difficult to remove by rinsing and shows up as a pattern in the final electroplate. Misting nozzles may be necessary to wet down the work to prevent this drying.

Electrode Effects; Current Density. Oxidation and reduction effects vary with the metal and usually determine whether cleaning should be anodic or cathodic. Metals which are passivated upon oxidation, such as nickel, stainless steel, or aluminum, are cleaned cathodically (aluminum is seldom electrocleaned). Brass is cleaned cathodically to avoid solution of the zinc component at the anode.

On the other hand, zinc (zinc base die casting) is cleaned anodically for another reason. Because of the sensitivity of the metal to attack by alkaline electrocleaners, it is desirable to use inhibited cleaners. When



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METAL CLEANING

silicate is used as an inhibitor, an insoluble film seems to develop when cleaning is cathodic. Hence, cleaning is anodic, with specially formulated cleaners, under mild conditions and for short times. Steel, which is relatively insensitive to oxidation-reduction effects, can be cleaned anodically or cathodically. At high current densities, there is a tendency toward browning of the steel unless an inhibitor (silicate or nitrate) is present in the cleaner. Stainless steel can also be cleaned either way although more drastic pickling action is required later when anodic cleaning is employed. The trend, in recent years, has been strongly towards anoxic cleaning of steel.

Experience has shown that good adhesion of electroplate is favored by anodic cleaning of the common ferrous metals. Cathodic cleaning is preferred for nickel and often has an activating effect when appropriate cleaner is used. Buffed nickel plate is electrocleaned cathodically before chrome plating. Copper parts or zinc die castings can be cleaned either way, but anodic cleaning is preferred to avoid deposition of films. Lead is usually cleaned cathodically to avoid anodic etching and staining. Brass is cleaned cathodically with a short reverse current stage preferred to desmut the surface.

Electrode effects are rather dependent on the current density. By convention, this is taken as amperes per square foot of surface area, presumably the surface area of both sides of the work. However, the current distribution and consequently the current density, is not uniform. It tends to be higher at edges and lower in recesses. The higher the current density, the greater is gas generation, metal dissolution, and cleaning. At very high current densities, detrimental dissolution and oxidation effects become more pronounced.

In many industrial establishments no effort is made to calculate the actual current density; this is especially true where parts are of irregular shape or vary from time to time. It is more common to measure the voltage and ignore the amperage, considering that with a constant resistance one is proportional to the other ($E=IR$). Electrocleaning is usually carried out at 3 to 6 volts. If the system cannot develop more than three volts, its resistance is too great for the generator and electrocleaning can be marginal; a cleaner of higher conductivity* should be used and the system examined for poor contacts or other mechanical difficulties.

* The role of the electrocleaner in determining the resistance of the system is important but not necessarily most important. The current must be carried through the bath by the charged ions; the mobility of the ions determines the efficiency of the current transfer. Monovalent ions such as potassium, sodium, chloride or hydroxyl, are more mobile than polyvalent ions like phosphate. The

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Current densities and times used most widely for the various metals are as follows:

Steel—50–150 amp/sq. ft	1/2 to 3 min
Brass—20–50 amp/sq ft	1/2 to 1 min
Zinc—10–30 amp/sq ft	20 sec to 1 min (see Chapter 7)
Nickel—20–80 amp/sq ft	1/2 to 2 min
Stainless steel—50–150 amp/sq ft	1/2 to 3 min
Aluminum—30–80 amp/sq ft	1/2 to 1 min
Copper—30–100 amp/sq ft	1/2 to 2 min

Tarnishing or darkening by the use of high current density in electrocleaning may be justified if the oxide is uniform and easily removed in an acid dip. This is often done deliberately on copper to avoid formation of red cuprous oxide which is insoluble in sulfuric acid, whereas the black cupric oxide is soluble.

Smut Removal. A major reason for the use of high current densities for steel is removal of smut. Smut may be the deposit left after pickling or etching, due to insoluble alloying elements such as ferric carbide. It may be due to carbonaceous deposits from decomposition of rolling or drawing lubricants during the rolling of sheet or forming of shapes, or subsequent heat treatment. It could be dust or finely divided abrasives entrapped in oil (rust preventive) left behind after degreasing, or atmospheric dust which settles on stored, oiled work. Removal of smut from steel is a very important problem in electrocleaning because of the widespread existence of this type of soil and its objectionable characteristic of impairing the quality of electroplate.

To blast off smut, it is desirable to have gas generation as great as possible. Hence, cleaners of high conductivity are used, at high concentrations (10 to 20 oz/gal), and at elevated temperatures (180 to 200° F)

hydroxyl ion is especially mobile so that the stronger alkalis, e.g., potassium hydroxide or sodium hydroxide are efficient current carriers and are present in high proportions in "high conductivity" electrocleaners. The ions are also more mobile at higher temperatures which are favored in electrocleaning for this reason as well as for enhanced detergency.

The relative effects of conductivity of the cleaner on cleaning have been assessed only qualitatively. The difference between a "high conductivity" and "low conductivity" electrocleaner might be 10 to 25% of the total resistance (in the author's estimation).

Other factors such as condition of the contacts on the rack or on the bus bars, variations in total surface area, shape of the parts as they influence current distribution, or surface films on the opposing electrode may be equally significant.

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so as to keep the internal resistance of the bath at a minimum and permit development of maximum current density.

With the greater generation of gas, selection of the type and concentration of surfactant is more significant; excessive foam should be avoided while retaining the foam blanket and detergency properties that are desirable. The surfactant is a definite asset, both in removal of the smut and preventing it from redepositing. If improper treatment is used, the smut is loosened and can be wiped off with a cloth, but it is not displaced during electrocleaning.

Some smuts can develop due to electrophoresis, the migration of colloidal particles to an electrode. Tiny insoluble particles of metal* or metal oxide may be carried by the colloid. The silicate content of smut-removing electrocleaners is maintained at a low level to reduce its colloidal nature.

Another source of difficulty due to migration of charged aggregates is caused by the use of the wrong surfactant. Thus, aggregates of soap derived from fatty acids or sodium resinate soaps tend to be attracted to the electrodes where they form films which both reduce conductivity and are difficult to remove by rinsing.

Even though soaps are not added to electrocleaners, they may enter the bath as part of the soil in the form of fatty acids or soap-containing emulsions or buffing compounds. Here is a good reason why either soak cleaners should precede the electrocleaner or two electrocleaning tanks should be used to reduce the effect of soap on the electrode (work part) in the final alkaline cleaning operation. Moreover, cleaning baths should be discarded and replaced at reasonable intervals when they become contaminated. If not, electroplating defects such as pitting or poor adhesion may result.

Chrome Contamination. After chromium plating, the metal deposited on the racks is normally stripped before the racks go back through the line. If this is not done, or if done incompletely, the chromium is dissolved in the cleaner and oxidized to the hexavalent state. Moreover, chromium is often stripped from the racks in the anodic cleaner. Another

* Tiny metal particles can cling to steel magnetized during fabricating steps, such as polishing or grinding. Moreover, the passage of electric current generates a magnetic field. This may be so strong that a piece of steel will be held on the side of the tank while the current is flowing. This magnetic field may cause steel shivers to be held more rigidly or may cause metal debris accumulated in the body of a cleaner to be picked up by the work piece. The remedy is a pressure spray, preferably with alkaline cleaner, to remove the metal particles by physical force. This is best done before electrocleaning.

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source of chromate contamination of the electrocleaner is the chromic acid that is trapped in cracks or holes of improperly maintained plating racks.

The effects of "chrome contamination" are often argued. It is quite likely that they are minimal in the anodic cleaning of steel, but quite significant in cathodic cleaning of steel where surface films can form that prevent good adhesion of electroplate. It is considered that the greatest effect of chrome contamination is the possibility of drag-over to the copper or nickel plating bath where chromium is very detrimental. Obviously, this is dependent on rinsing and can be avoided.

Hexavalent chromium can be reduced to the trivalent state, a form which appears to be less harmful, by the addition of small amounts, e.g., 1/2 to 1 oz./gal. of sodium bisulfite, hydrosulfite, or metabisulfite. This effect is a transient one as the reducing power of the sulfite is lost and the chromium reoxidized at the anode. Eventually, excessive quantities of reducing agent are required and it is cheaper to discard the bath.

Cleaning in the Strike Bath. A cyanide strike bath is often used after cleaning and serves as an intermediate between preparation of the metal and the major electroplating. The strike bath is deliberately inefficient with regard to plating. Its objective is to prevent formation of a loosely held deposit due to galvanic action. The limited amount of metal deposited (copper, nickel, or silver) is well bonded to the base metal.

The cyanide strike (or cyanide dip when no metal is deposited) serves both as a cleaner and surface conditioning step. The cyanide has a high alkali concentration and sometimes trisodium phosphate is added to improve cleaning. The cyanide beneficially forms complexes with unwanted metal ions. Very occasionally the acid oxide removal and conditioning step is omitted; the electrolytic cyanide bath removes the oxide formed during cleaning.

It is not good practice to depend upon the cyanide strike to provide cleaning. Rather it is to be considered as a safety measure. Certainly less trouble is experienced when it is present. If it becomes contaminated, on the other hand, it can be dangerous, being too close to the electroplating bath with usually no rinse between the strike and plating bath. J. B. Mohler* suggests making the alkaline electrocleaner a strike bath by addition of sodium stannate.

"Steam Cleaning" with Detergent

This method delivers a hot detergent solution mixed with some steam under considerable pressure through a gun-like tube ending in a relatively

* *Metal Finishing*, p. 69, (March 1958).

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